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The wastewater treatment in the biodiesel production with alkali-catalyzed transesterification

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ABSTRACT

Biodiesel has been studied in last few decades because of limited energy resources and a huge increase of the energy demand. The basic feedstocks for the production of biodiesel are vegetable oils and animal fats that contain primarily triacylglycerols while the main reaction is transesterification. This reaction is most frequently conducted at commercial scale in the presence of the homogeneous alkali catalyst. Previous studies on biodiesel were mainly focused on its production and fuel properties, while its environmental management is rarely considered. The present work is a review of the previous studies on treating wastewaters generated by the biodiesel production processes involving alkali-catalyzed transesterification. The attention is focused on physical, chemical, physico-chemical, electrochemical, biological and integrated treatment processes of biodiesel wastewaters. Both advantages and disadvantages of different biodiesel wastewater treatment processes are discussed. Since different input biodiesel wastewaters are employed in different studies, it is difficult to compare different treatments with respect to their contaminant removal efficiencies. Proper acidification and chemical coagulation/flocculation or electrocoagulation remove grease and oil successfully but they are unsuccessful in removing COD. The combinations of acidification, coagulation and the electrochemical treatment improve the removal efficiencies of COD and BOD. Advanced oxidation technologies appear not to be effective in removing the contaminants from raw biodiesel wastewaters. The performance of biological processes is improved by the pretreatment of biodiesel wastewater with acidification, chemical coagulation, electrocoagulation or photo-Fenton. When selecting a treatment process, it should be evaluated with respect to its treatment efficiency and operational requirements. The right choice is probably an integration treatment involving acidification, coagulation/flocculation or electrocoagulation and a biological process. The reuse of the pretreated wastewater is also an interesting alternative.

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1. Introduction

A huge increase of the energy demand in the world, the continuing rise in energy costs, limited resources of petroleum, as well as the pollution problems caused by the wide use of petroleum-based fuels have encouraged recent interests in alternative energy resources. During the past decade the world's oil consumption increased from 3640.2 million tonnes in 2002 to 4130.5 million tonnes in 2012 with an average annual growth rate of about 1.3% [1]. Also, the petroleum-based fuel production increased from 3602.7 million tonnes in 2002 to 4118.9 million tonnes in 2012. However, petroleum is a limited resource with the proved world reserve of 1668.9 billion barrels at the end of 2012, which is sufficient to meet about 53 years of the global production. Therefore, the world is on the verge of an energy crisis and a growing concern on the alternative energy sources has received a great attention. Among the alternative energy sources, bio-based fuels, especially biodiesel, remain an option but face difficult challenges, particularly in meeting quality specifications and the

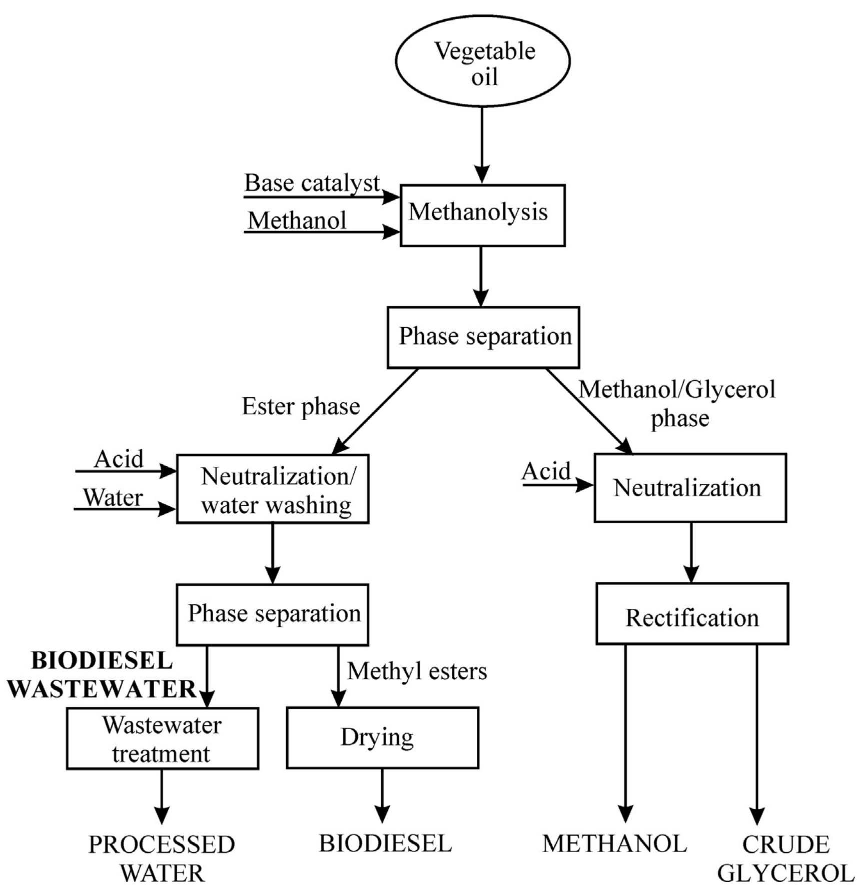

Fig. 1. Schematic presentation of biodiesel production process based on alkali-transesterification of oily feedstocks.

Table 1
Parameters of biodiesel wastewaters from different biodiesel production processes.

Parameter	[11]	[13]	[8]	[12]	[20]	[21]	[22]	[23]	[24]	[25]	[26]		[27]	
Color, Hazen unit									> 500		> 500[a]	> 500[b]		
pH	11.0	10.44	6.7	8.9	9.25–10.75	8.5–10.5	10.2	10.3	10.1	11.11	11.11	11.21	5.9[c]	3.3[d]
COD, g/L		16.564	18.362	30.98	312–589	60–150	542.4	56.4	160	17.75	3.681	40.975	10.85	43.90
BOD, g/L		ND			168–300	30–60	224.63		103	7.98	1.600	15.260		
Grease and oil, g/L	15.1	0.5		6.02	18–22	7–15	21.05	3.3			0.387	0.459	12.0	21.0
Oily sludge, g/L						1,5–5								
Carbon, g/L	14.8								48	6.62	1.700	6.495		
Nitrogen, mg/L	64.7				439–464			14						
Total phosphorus, mg/L								ND					3,450	3,199
Conductivity, μS/cm			1119	350					1133	758			43,100	44,306
Total suspended solids, g/L	2.67		8.85	0.34				0.4					0.512	0.527
Chloride, g/L													14.27	13.53
Sulfate, mg/L													57.0	56.2
Methanol, g/L				10.67				40.3	0.254	0.315	0.315	0.225		
Glycerol, g/L				1.36				2.4						
Volatile suspended solids, g/L			8.75											
Mineral suspended solids, g/L			0.1											
Saponification value, mg KOH/g						4.77–18.79								
Free fatty acid, % palmitic acid						0.14								

[a] Biodiesel produced from palm oil.
[b] Biodiesel produced from castor oil.
[c] Low-loaded wastewater WW1.
[d] High-loaded wastewater WW2.

environmental issues. The production of biodiesel, the only biofuel that can be used for the diesel engine, has steadily increased during the last years. The world biodiesel production in 2007 was 24,000 t/d but it reached 55,000 t/d in 2011 [2].

Chemically, biodiesel is a mixture of mono-alkyl esters of fatty acids confirming a quality standard (EN14214). Compared to petroleum diesel, biodiesel is biodegradable and essentially non-toxic, produces lower emissions and has a higher flash point. Biodiesel can be used in blends with petroleum diesel, with minimal or without engine modification. Generally, biodiesel can be produced from renewable resources (edible and non-edible vegetable oils and animal fats) by the reactions of transesterification and esterification of triacylglycerols and free fatty acids, respectively. In both reactions, an alcohol (most often methanol or ethanol) is added in an excess to shift the equilibrium to the right. To increase their rates, these reactions are usually catalyzed by an acid, a base or an enzyme although they can be carried out at high temperatures and pressures in the absence of any catalyst. Since the basic feedstocks for the production of biodiesel are vegetable oils and animal fats that contain primarily triacylglycerols, transesterification is the main reaction for the biodiesel production. This reaction is most frequently conducted at commercial scale in the presence of a homogeneous base catalyst (alkali hydroxide or alkoxides). This method enables a high yield of biodiesel from triacylglycerols in a relatively short time.

A typical biodiesel production process based on alkali-transesterification of oily feedstocks is shown in Fig. 1. The main process steps are as follows: transesterification reaction, the separation of the ester phase (crude biodiesel) from the methanol/glycerol phase, wet washing of the ester phase, the separation of biodiesel from wastewater and drying of biodiesel. The process also involves the processing of the crude glycerol phase through acidification and the separation of glycerol from alcohol. The purification of crude biodiesel and the recovery of the excess alcohol and glycerol are desirable to improve the biodiesel quality and to reduce the biodiesel production costs.

The methyl esters produced by transesterification can be classified as biodiesel only if the standard specifications, such as EN 14214, are fulfilled. Therefore, the purification stage is essential for the practical application of produced methyl esters (crude biodiesel). Ineffective crude biodiesel purification can cause problems in the operation of a diesel engine such as plugging of filters, coking on injectors, engine knocking and so on [3]. A number of technologies for the purification of biodiesel are commercially available, novel technologies are also emerging. A few reviews on the purification of crude biodiesel have been recently reported [4,5].

For purifying crude biodiesel two methods are generally applied: wet washing and dry washing. Relatively expensive membrane separation technologies are also tested for biodiesel purification [6], but yet, it is a less convenient method than wet washing [7]. Wet washing is more traditional and widely used for removing excess contaminants and leftover production chemicals from biodiesel. Dry washing uses an ion exchange resin or a magnesium silicate powder to remove impurities. Both wet and dry washing methods are being used at commercial scale, but only wet washing resulted in the purified biodiesel that fulfilled the requirements of EN 14214 Standard [8]. The washing with hot, distilled water (50 °C) results in the biodiesel purity of 99% [9].

The wet washing method yields wastewater, called biodiesel wastewater, containing the unreacted oil or fat, remained catalyst, salts, soaps and organic impurities. Biodiesel wastewaters can be hazardous to the environment and must not be disposed into sewage systems, rivers or lakes without a prior appropriate treatment. Since the biodiesel manufacturing process results in about 0.2–3 L of the biodiesel wastewater per liter of the produced biodiesel, the world generation of the biodiesel wastewater in 2011 is estimated to be 13,000 to 193,000 m^3/d. Therefore, the environmental and economic importance of treating biodiesel wastewaters is extremely high because of their high pollution levels and volume.

Besides the biodiesel wastewater, the biodiesel production plant generates the additional wastewater streams from other areas including the steam condensate, the wastewater from the process water softening, the water used for washing the equipment and floors and sanitary wastewater. Since only the biodiesel wastewater treatment is the concern of the present paper, the treatment of these additional wastewaters will not be considered.

Most of the previous studies on biodiesel were focused on its production and fuel properties, while its environmental management has been rarely considered. However, the literature sources have currently shown the increase in the potential need for the

Table 2
Comparison of removal eficiency of biodiesel wastewater treatment.

Type of treatment	Biodiesel wastewater		Removal efficiency, %						Ref.
	Origin[a]	Parameters[b]	COD	BOD	G&O	TSS	MeOH	Glycerol	
Physico-chemical	Model (aqueous glycerol solution)	Glycerol						32.6	[32]
Adsorption (coconut activated carbon)		(10 mg/L)						46.4[c]	
Physico-chemical	Raw (LS, ACT, MeOH, alkali)	COD 9,595–54,362	90	76	67				[33]
Adsorption (commercial chitosan flakes)		BOD 1492–2286							
		G&O 1040–1710							
Physico-chemical	Raw (CS, ACT, MeOH, NaOH)	COD 16.564							[13,34]
Neutralization		G&O 0.5	26		10				
Neutralization + filtration through sand and gravel			38		20				
Neutralization + filtration through sand, gravel and membrane			41		20				
Coagulation by ferrous sulfate			63		100				
Coagulation by aluminum sulfate			69		100				
Physico-chemical	Raw (CS, ACT, palm oil)	COD 60-150							[35,36]
Acidification (sulfuric acid, pH 3)		G&O 7-15			95				
Coagulation ($FeCl_3$, 0.5 mg/L; pH 5)		TSS 1.5-5	60		97	97			
Coagulation ($FeCl_3$, 0.5 mg/L; coagulant aid, 0.5-0.75 mg/L; pH 7)					97				
Coagulation (polyaluminum chloride)			70		99	97			
Physico-chemical	Raw (CS, ACT, MeOH, waste cooking oil)	COD 542							[22]
Acidification (pH 6) + coagulation (aluminum sulfate, 2 g/L)		BOD 225	98.8	98.7	99.5	45.6			
Acidification (pH 4) + coagulation (polyluminum chloride, 1 g/L)		G&O 21.1	98.0	98.0	99.1	56.5			
		TSS 30.5							
Physico-chemical	Raw (CS, ACT, palm oil)	COD 60-150							[21]
Acidification + coagulation with air floatation		G&O 7-15	80–90	80–90	98–99.6	98–100			
		TSS 1.5-5							
Electrochemical	Raw (CS, ACT, waste cooking and crude palm oils)	COD 30.98							[12]
Electrocoagulation (aluminum and graphite electrodes; pH 6; 20 V; 25 min)		G&O 6.02	55.4		97.8	96.9	16.9	3.5	
		TSS 0.34							
		MeOH 10.7							
		Glycerol 1.36							
Electrochemical	Raw (CS, ACT, waste cooking and crude palm oils)	COD 30.98							[37]
Electrocoagulation (aluminum and graphite electrodes; pH 6.06; 18.2 V; 23.54 min)		G&O 6.02	55.0		97.5	97.0			
		TSS 0.34							
Electrochemical	Raw (LS, ATC, cotton oil)	G&O 9.5							[38]
Electrocoagulation/floatation (aluminum electrodes; pH 2.5–7.9; 3.5–4.8 V; 20–60 min)		TSS 6.5			97.9–99.8	57.5–88.0			
Electrochemical	Model (aqueous solution of glycerol, methanol, NaOH, oleic acid)								[39]
Hydrothermal electrolysis (batch; 1 A; 250 °C; 90 min)								83	
Hydrothermal electrolysis (continuous; 1 A; 280 °C; 60 min)								75	
Coupled chemical and electrochemical	Raw (CS)	COD 22.5							[40]
Electrocoagulation (iron electrodes)		G&O 6.412	47.6		83.0				
Electro-coagulation + polyaluminum chloride (0.5 g/L)			70.0		94.0				
Electro-coagulation + hydrogen peroxide (2 %)			81.2		99.7				
Electro-coagulation + polyaluminum chloride (0.5 g/L) + hydrogen peroxide (2 %)			94.1		100				
Coupled chemical and electrochemical	Raw (CS, waste cooking oil)	COD 312							[20]
Acidification (sulfuric acid; pH 2-6)		BOD 168	40–74	13–24	87–98				
Acidification (sulfuric acid) + electrooxodation (Ti/RuO2 electrodes; 0.061 M NaCl)		G&O 18	100	95	100				
Coupled chemical and electrochemical	Raw (CS, vegetable oil)	COD 312							[41]
Acidification (sulfuric acid)		BOD 168	38.9	76.3	99.4				
Acidification (sulfuric acid) + coagulation (aluminum sulfate, 2 g/L; pH 6)		G&O 18	97.5	98.6	98.9				
Acidification (sulfuric acid) + electrocoagulation (iron electrodes; pH 7.4; 12.42 A; 4 h)			99.6	91.5	98.7				

Table 2 (*continued*)

Type of treatment	Biodiesel wastewater		Removal efficiency, %						Ref.
	Origin[a]	Parameters[b]	COD	BOD	G&O	TSS	MeOH	Glycerol	
Advanced oxidation technology	Raw (LS, ATC, MeOH, KOH, palm oil)	COD 6.62							[25]
Electrooxidation (diamond and zirconium electrodes; 0.04 A; NaCl, 2.5 g/L)			9.0				27.5		
Ozonation (ozone 0.34 g/L; pH 12)			5.0				14.4		
Advanced oxidation technology	Raw (LS, ACT, MeOH, KOH, palm oil)	COD 160							[24]
Heterogeneous catalysis (TiO_2 Degussa 25 immobilized on silica; hydrogen peroxide, 1 mL/L; 0.68 mL/min; high pH)			3.0[d]				15.3[d]		
Photo-Fenton (ferrous sulfate, 0.3 mM; hydrogen peroxide, 35 mM)			80.3[d] 7.0				99.5[d] 23.8		
Biological	Raw, diluted 1:1, enriched (CS, ACT, KOH, waste oil)	G&O 15.1			98				[11]
Rhodotorula mucilaginosa (pH 6.8; urea C/N ratio, 17-68; yeast extract, 1 g/L)									
Biological	-	COD 60 BOD 2.9 G&O 120	99	98	99				[42]
Integrated chemical and biological	Raw (CS, ACT, MeOH, waste cooking palm oil)	COD 56.4							[23]
Pretreatment step: acidification (sulfuric acid; pH 4) + coagulation (polyaluminum chloride, 62.5 mg/L; cation polymer, 1.25 mg/L)		G&O 3.27 MeOH 40.3	22		96	84	12	6	
Biomethanization (anaerobic baffled reactor; 1.5 g/m^{3}d COD)		Glycerol 2.4	99			84	100	100	
Integrated chemical/electrochemical and biological	Raw (CS, ACT, MeOH, waste cooking oil)	COD 428							[43]
Pretreatment step:			63						
Acidification (sulfuric acid, pH 4) + coagulation/ flocculation (aluminum polychloride, 18%, 0.2 mL/L; Actipol A-401, 1 g/L)									
Acidification (sulfuric acid, pH 4) + electrocoagulation (aluminum electrodes; 12 V, 1.5 A, 30 min)			45						
Biomethanization (anaerobic stirred reactor; granular sludge)	Coagulated pretreated wastewater		84						
	Electrocoagula-ted pretreated wastewater		98						
Integrated primary chemical sedimentation + biological + secondary chemical sedimentation + reverse osmosis	Raw, low- (WW_1) and high- (WW_2) loaded	COD 10.85,[g] 43.90[h]							[27]
Coagulation/flocculation (Polfloc M92, polyaluminum chloride, anionic polymer, pH 7-8)			28.6[g], 16.3[h]						
Coagulation/flocculation + trickling filtration			62.9[g], 79.4[h]						
Coagulation/flocculation + activated sludge			67.5[g], 74.7[h]						
Coagulation/flocculation + trickling filtration + activated sludge + secondary coagulation/ flocculation			92.1[g], 94.3[h]						
Coagulation/flocculation + activated sludge + secondary coagulation/flocculation + reverse osmosis			92.8[i]						
Integrated photo-Fenton and biological	Raw (LS, ACT, MeOH, KOH, palm oil, castor oil)	COD 3.68,[e] 40.98[f]							[26]
Photo-Fenton (pH 2.3; ferrous sulfate 0.3 mM; hydrogen peroxide 35 mM)		BOD 1.6,[e] 15.26[f] G&O 0.39,[e] 0.46[f]	23[e], 29[f]	34[e], 28[f]	59[e], 42[f]		24[e], 29[f]		
Activated sludge process (aerobic sequential batch reactor)		MeOH 0.315,[e]	90[e]						
Coupled photo-Fenton/aerobic sequential batch reactor		0.225[f]	90[e], 76.1[f]	90[e], 69[f]					

[a] CS – commercial scale; LS – laboratory scale. ACT – alkali-catalyzed transesterification. MeOH – methanol; EtOH – ethanol.
[b] COD – chemical oxygen demand (g/L); BOD – biochemical oxygen demand (g/L); G&O – grease and oil (g/L); TSS – total suspended solids (g/L); MeOH -methanol (g/L.); Glycerol (g/L).
[c] Thermally treated activated carbon.
[d] Five times diluted raw biodiesel wastewater.
[e] Palm oil.
[f] Castor oil.
[g] WW1.

biodiesel wastewater treatment. The literature review reveals that physical, chemical, physico-chemical, electrochemical, biological and integrated treatment processes have been applied since 2005 when the first works on biodiesel wastewater treatments were reported. Thus, it is evident that the biodiesel wastewater treatment is a new area of research that is beginning to be developed. Two reviews on biodiesel wastewater treatment have been recently reported. Palomino-Romero et al. [10] presented a summary on both various treatment processes for removing the pollutants from biodiesel wastewaters and the recovery, reuse, energy production and synthesis of new compounds from side-streams of the biodiesel production process. Kolesárová et al. [7] reviewed possible uses of byproducts (crude glycerol, oil cakes and wastewater) from the biodiesel production for obtaining biogas by anaerobic digestion. However, neither of the two reviews has considered all processes for the biodiesel wastewater treatment reported so far. Therefore, the aim of the present work was to give a more complete review of the published processes for treating the wastewater generated in biodiesel production plants based on alkali-catalyzed transesterification than the previous ones. These methods are compared with respect to their efficiencies in removing the usual contaminants. Other possible uses of biodiesel wastewaters are also discussed.

2. Wet washing – a purification step in the biodiesel production process

In order to remove soluble impurities such as residual catalyst, methanol, soap and glycerol, wet washing of crude biodiesel can be conducted by using:(a) deionized water, (b) mineral acid and water and (3) organic solvents and water [5]. Before the wet washing step, the excess of alcohol is sometimes separated by distillation. Advantages and disadvantages of different crude biodiesel purification technologies have been discussed in detail elsewhere [5].

Water washing is most often used for purifying crude biodiesel after being separated from the glycerol phase. This method includes the addition of hot water to crude biodiesel under gentle agitation to prevent the emulsion formation. If hot distilled water is employed for washing, precipitation of saturated biodiesel is eliminated and the emulsion formation is prevented. After settling and separating the aqueous phase, fresh water is added to the washed biodiesel. The washing is usually repeated several times (2–5 times) until colorless spent washing water (biodiesel wastewater) is obtained, meaning that the impurities are completely removed. A large amount of the biodiesel wastewater is generated by the water washing step, depending on the washing method applied. The researchers have reported different amounts of the biodiesel wastewater generated in biodiesel production plants (per 100 L of biodiesel produced), for instance 20 L [11], 20–120 L [12] and 300 L [13]. Some other amounts of the biodiesel wastewater have been also reported such as about 10% [14] and 47.5% [15] of the biodiesel produced. The waste oil technology demands the acid pre-treatment of feedstock and produces twice higher amounts of wastewater [16–18]. The amount of hot water for biodiesel washing can be minimized by neutralizing the remaining alkali catalyst using phosphoric acid [19]. The reduction of the total water consumption can be done by recirculating an extent back to the process.

Biodiesel wastewater is a viscous liquid with an opaque white color. It is alkaline and contains a high content of residual oil, soluble salts (chloride and sulfate), remained catalysts, soaps and organic impurities (free fatty acids, methyl esters, acylglycerols, methanol and glycerol). However, the content of nitrogen and phosphorus is extremely low [11]. Many researchers have reported biodiesel wastewater characteristics, such as pH (3.3–11.2), chemical oxygen demand (COD, 11–590 g/L), biologic oxygen demand (BOD, 1.6–300 g/L), grease and oil (0.4–22 g/L), total organic carbon (TOC, 1.7–40 g/L), total suspended solids (0.3–8.9 g/L), etc. Table 1 shows the ranges of important parameters of biodiesel wastewaters applied in previous studies. It is obvious that the biodiesel production system strongly influences the characteristics of the biodiesel wastewater.

In addition to a high purity level of biodiesel, wet washing offers several disadvantages such as the increased cost and production time, the generation of highly polluted wastewater and a significant loss of biodiesel. The costs of the wastewater treatment are estimated to be 0.12–3.6% [28] 3.8% [29], 0.14% [30] and 0.09–3.8% [31] of the total production cost for approximately 8 million tonnes of the annual biodiesel plant capacity. However, this stage cannot be avoided because the purity level of the biodiesel strongly affects fuel properties and engine life. In particular, the presence of acylglycerols in biodiesel fuel causes serious problems in application [9]. Purified biodiesel should be properly dried by hot air to eliminate water, so it can be immediately used on diesel engines or safely stored.

Despite the residual oil, this wastewater is considered to be unfavorable for microbial growth [11]. Except for the carbon source, nutrients for microbial growth, such as nitrogen and phosphorous compounds, are not abundant in the biodiesel wastewater. Due to the presence of inhibitor(s) of microbial growth, biodiesel wastewater can be hard to degrade naturally.

3. Biodiesel wastewater treatment processes

Biodiesel wastewaters should not be discharged into the public sewerage system where the residual oil can cause problems, such as the reduction of the microbial activity and plugging of the system. To protect the environment, the wastewater from a biodiesel plant should be adequately treated prior to disposal or reuse. Biodiesel wastewaters are highly stable emulsions containing grease, oil and soap, so the treatment by a grease trap tank is ineffective. This wastewater has an alkaline pH, which required an effective treatment to be reduced to the level that favors the subsequent stages of processing. Also, in most cases, an upstream chemical–physical pretreatment is required to achieve a good efficiency and effective operation of the biological treatment. Moreover, the reuse of all process wastewaters in the production of biodiesel is an interesting option for the factory management. A typical treatment process for reusing the wastewater should include the use of a physico-chemical process followed by floatation or sedimentation, a biological treatment and a reverse osmosis system.

Several treatment processes have been developed for the wastewater generated by the biodiesel production via alkali-catalyzed transesterification such as: (a) physico-chemical treatments, (b) electrochemical treatments, (c) coupled chemical and electrochemical treatments, (d) advanced oxidation technologies, (e) biological treatments and (f) integrated treatment including previous treatment processes. Table 2 reviews various biodiesel wastewater treatments reported since 2005.

3.1. Physico-chemical treatments

The physico-chemical treatment of the biodiesel wastewater involves adsorption, acidification (pH adjustment) and flocculation/coagulation processes or their combination, eventually followed by a physical treatment such as sedimentation, filtration or floatation. This method assumes the addition of appropriate chemicals that adjust the pH value, cause coagulation and favor

Table 3
Efficiency of different physico-chemical methods for treatment of biodiesel wastewater.[a]

Parameter	Removal efficiency, %				
	Neutralization	Neutralization followed by filtration through sand and gravel	Neutralization followed by filtration through sand, gravel and membrane	Coagulation/ flocculation by ferrous sulfate	Coagulation/ flocculation by aluminum sulfate
Color	27	31	83	100	100
Turbidity	5	17	0	100	100
COD	26	38	41	63	69
Hydrocarbons	16	22	29	100	100
Grease and oil	10	20	20	100	100

[a] Adapted from De Boni et al. [13] and Goldani et al. [34].

flocculation. The primary task of the chemicals added is to destabilize the oil-in-water emulsion and to form flocs that will agglomerate and easily settle. The method is usually conducted as a pretreatment step before the conventional biological treatment.

3.1.1. *Adsorption*

Adsorption is a surface-based process that creates a film of pollutant molecules on the surface of the solid particles (adsorbent) suspended in a stirred tank or packed in a column. The type of bonding depends on the nature of the species involved. The adsorption of pollutants from biodiesel wastewaters is based on physical interactions between the adsorbent surface and pollutant molecules [32,33].

Adsorption, as other physical treatment operations, is almost not used alone for treating biodiesel wastewaters. There are a few reports dealing with this method describing the use of adsorption for removing pollutants from biodiesel wastewaters [32,33]. Rather physical methods, such as floatation and sedimentation, are combined with other treatment methods.

Liu et al. [32] studied the glycerol removal from model biodiesel wastewaters by adsorption on various adsorbents (activated carbons, natural and synthetic zeolites and clays) at room temperature in order to find a cheap and efficient one for treating real biodiesel wastewaters. For activation, the adsorbent materials were thermally pretreated according to a specific temperature regime before use. The adsorption of glycerol from aqueous solutions was carried out within 24 h of shaking. Among the examined adsorbent materials, the activated carbons showed the best adsorption for glycerol. The models of the Langmuir isotherm and the first-order desorption kinetics were confirmed for adsorption of glycerol on the coconut activated carbon by fitting the experimental data.

Pitakpoolsil and Hunsom [33] used commercial chitosan flakes as an adsorbent for removing pollutants from wastewater generated at the laboratory-scale biodiesel production plant involving used vegetable oil, methanol and an alkali catalyst. The effect of the adsorption time, initial pH, the dosage of adsorbent and mixing rate on the adsorption capacity and removal efficiency of pollutants were explored. Under the optimal adsorption conditions (the initial pH of 4.0, the adsorption dosage at 3.5 g/L, agitation speed of 300 rpm and the adsorption time of 3 h), the reduction of the initial levels of BOD, COD and grease and oil were 76%, 90% and 67%, respectively. The treated wastewater with a satisfactory quality level was obtained after the fourth repetitive adsorption cycle. The adsorption equilibrium of all pollutants onto chitosan flakes fitted with the Langmuir isotherm. The adsorbent can be regenerated with 0.2 M NaOH, but the adsorption capacity decreased with increasing the number of regeneration.

3.1.2. *Acidification*

Acidification is usually used as a pretreated stage prior to chemical or other treatment of biodiesel wastewaters. This means the pH adjustment by adding an acid to destabilize and destroy emulsion of oil in biodiesel wastewater in order to separate the oily impurities or to recover residual oil and free fatty acids before the coagulation process. The demulsification is achieved by reducing electric forces or destroying electrical double layer which allows the coalescence of fine oil drops into larger ones. The pH adjustment can change a chemical structure of the functional group, reducing the emulsion stability. Acidification also breaks up the soaps into a salt and a free fatty acid. Different chemicals were used to adjust the pH of the biodiesel wastewater before the coagulation process, such as acids [13,22,34–36] or calcium oxide [22].

3.1.3. *Coagulation/flocculation*

The demulsification of oil-in-water emulsion can be achieved with the coagulation/flocculation by adding a coagulant, an inorganic salt (e.g. ferry chloride or aluminum sulfate) or a pre-polymerized inorganic compound (e.g. polyaluminum chloride). Coagulation and flocculation occur in successive steps. When a coagulant is added to the biodiesel wastewater, metal ions hydrolyze rapidly, forming a series of metal hydrolysis products. In the first step, the forces stabilizing the formed particles (flocks) are overcome by neutralizing their charges. A vigorous mixing is needed to achieve good coagulation. Fine particles are then flocculated under the conditions of gentle mixing that favors the formation of large flocs that rapidly settle or float. The pH adjustment can enhance the efficiency of coagulation by inorganic salts. The formed metal hydroxide enmeshes suspended particles and sweeps down or up. This sweep coagulation can be enhanced by using some organic polymers as a coagulant aid that enlarges flocs.

Coagulation/flocculation preceded by pH adjustment is frequently used in the physico-chemical treatment of biodiesel wastewaters. Both aluminum and iron salts are commonly used as a coagulant. A common sequence of operations is as follows: pH adjustment, coagulation/flocculation and sedimentation or floatation.

De Boni and coworkers [13,34] studied several methods to treat the wastewater from the water washing of crude biodiesel obtained from soybean oil by NaOH-catalyzed transesterification using methanol. The methods included (a) the pH neutralization with an acetic acid solution (0.01%) and hot water washing with or without subsequent filtration through gravel and sand or gravel, sand and a membrane between the layers, and (b) the coagulation/flocculation using either ferrous sulfate or aluminum sulfate. Table 3 shows the removal efficiencies of the color, turbidity,

Table 4
Parameters of wastewaters treated by the two-step treatment process.[a]

Parameter	Biodiesel wastewater	Removal efficiency, %		
		Wastewater after the first step (acidification)	Wastewater after the second step (coagulation/flocculation)	
			Aluminum sulfate	Polyaluminum chloride
COD, g/L	542.40	47.0–50.0	98.8	98.8
BOD, g/L	224.63	70.0–97.0	98.7	98.0
Grease and oil, g/L	21.05	98.0–99.0	99.5	99.1
Total dissolved solids, g/L	30.53	42.7–43.3	45.6	56.5

[a] Adapted from Kumjadpai et al. [22].

COD, hydrocarbons and greases and oils achieved by the applied methods. The methods involving neutralization with or without filtration were not efficient in the wastewater treatment except for turbidity and color when the neutralized wastewater was filtered through gravel, sand and the filtering membrane. The similar and sufficient removal efficiencies of all the parameters except the COD value were achieved by using coagulants, ferrous sulfate and aluminum sulfate, at the optimum dosage (1.90 g/L and 1.45 g/L, respectively). The modest removal of COD (below 70%) meant that some components of the wastewater, such as methanol and glycerol, could not be removed by the chemical treatment applied. The authors claimed that the chemical coagulation/flocculation treatment was economically feasible, as for an industrial plant with the biodiesel production of 100,000 L/d the cost of the biodiesel wastewater treatment would not reach 0.7% of the annual turnover of the company. Also, the pretreated wastewater could be reused in the process.

Sawain et al. [35,36] studied the destabilization and demulsification of the wastewater from the biodiesel production from palm oil by adjusting the pH value and using aluminum salts (aluminum sulfate and polyaluminum chloride), ferric chloride and a cationic polymer as a coagulant aid. The pH adjustment influenced the emulsion, and grease and oil and soap were easily separated from the water at pH $\leq$ 3. Because of a low pH value, only the pH adjustment may not be appropriate for the subsequent biological treatment. Therefore, the use of coagulants was tested at the controlled pH value. Coagulation by aluminum sulfate and polyaluminum chloride was highly efficient for the wastewater demulsification at pH = 5. Aluminum sulfate removed 97%, 60% and 97% of grease and oil, COD and suspended solids, respectively, while 99% of grease and oil, 70% of COD and 97% of suspended solids were removed with polyaluminum chloride [34]. Having a lower cost, aluminum sulfate was recommended for practical use. Ferric chloride or ferric chloride with the cationic polymer solution (20%) resulted in 97% of total removal of grease and oil, COD and suspended solids at the controlled pH value in the range between 5 and 6 [35]. The wastewater was firstly vigorously agitated (100 rpm) for 1 min to enable a fast coagulation, followed by slow agitation (30 rpm) for 20 min to favor flocculation and subsequent sedimentation.

Kumjadpai et al. [22] used a two-step process to purify a wastewater from the conventional biodiesel production from the waste used oil, which did not have a stage for neutralizing the crude biodiesel. The wastewater was collected from the washing unit after the glycerol and methanol separation and was alkaline. The first treatment step involved the acidification of the wastewater by adding concentrated sulfuric, nitric or hydrochloric acid and resulted in the crude biodiesel recovery. In the second treatment step, the aqueous phase generated in the first step was treated by chemical coagulation/flocculation using aluminum sulfate or polyaluminum chloride. Prior to coagulation, the aqueous phase was adjusted to within the favorable pH range (for aluminum sulfate: pH 4.5–10; for polyaluminum chloride: pH 2.5–7.0) by adding calcium oxide. The coagulation/flocculation was carried out with agitation for 1 min at 300 rpm and for 20 min at 40 rpm. The results of the two-step treatment process are shown in Table 4.The removal efficiencies of COD, BOD and grease and oils were comparable to those achieved in the biological treatment of Suehara et al. [11] and Kato et al. [42].

When a mineral acid was added to the biodiesel wastewater in the first-step treatment, two layers were automatically separated, the upper layer being richer in methyl esters and the lower layer being the aqueous phase. Most of methyl esters were recovered at pH values of 1.0 and 2.5 within the first 7 min with all three acids. The recovering efficiencies (in mL of methyl esters per liter of wastewater) of 25–30, 15–17 and 19–21 were achieved with sulfuric, nitric and hydrochloric acid, respectively. All three acids removed nearly 100% of grease and oil at pH 1.0, but sulfuric acid was more efficient in removing COD and BOD at pH 1.0–2.5 than the other two acids. Therefore, sulfuric acid was selected as the optimum acid for recovering methyl esters from the biodiesel wastewater [22].

The coagulation/flocculation with aluminum sulfate or polyaluminum chloride as the second-step treatment was tested in a range of 0–10 g/L at the pH values between 4.5 and 10, which was adjusted by adding calcium oxide [22]. Since calcium oxide acted as a coagulant, the removal efficiencies of COD, BOD and grease and oil in the presence of only calcium oxide increased with increasing the pH value of the treated wastewater. The addition of aluminum sulfate or polyaluminum chloride increased the removal efficiency of all parameters analyzed (Table 4). The optimum dosages of aluminum sulfate and polyaluminum chloride were 2 g/L at pH of 6.0 and 1 g/L at pH of 4.0, respectively. However, a lower amount of sludge was generated with aluminum sulfate than with polyaluminum chloride. Also, the use of aluminum sulfate was cheaper than that with polyaluminum chloride for 0.22 US\$/m^3. According to Kumjadpai et al. [22], the operating cost of the developed two-step treatment system was significantly cheaper than that of a conventional procedure (incineration), but it would require biological remediation in sedimentation ponds to reduce the pollutant levels to acceptable limits.

3.1.4. *Dissolved air floatation*

The dissolved air floatation is one of the methods employed for treating the wastewater from the biodiesel production before the biological treatment [21,38]. This method is known as effective for removing solid particles of low density from suspensions and clarifying low turbidity. Also, it is successful for separating oily materials from aqueous emulsions after the chemical pretreatment.

Dissolved air floatation is a physical operation that removes dispersed oil drops or solids by dissolving compressed air in the biodiesel wastewater and then releasing the air at atmospheric pressure. Tiny air bubbles that are formed adhere to oil drops and solids causing the dispersed matter to float to the free surface where it is then removed by a skimmer. The biodiesel wastewater may require pre-treatment by coagulation/flocculation stages. The pH adjustment may also be considered to ensure the optimum conditions for coagulation and flocculation.

Rattanapan et al. [21] studied the purification of the wastewater from an alkali-catalyzed transesterification process which

had high levels of COD and grease and oil (Table 1). They tried to enhance the efficiency of the dissolved air floatation for treating the biodiesel wastewater by acidification and coagulation. Firstly, the wastewater was acidified with pure hydrochloric or sulfuric acid while the mixture was agitated at 30 rpm for 20 min. At pH 3.0 and one day retention, the grease and oil level was reduced for more than 80%, while the COD removal was only 50%. The removal efficiency of grease and oil increased with the increase of the retention time, reaching a level of more than 95% within 5 days. The efficiencies of the two acids at pH 3 and one day retention were equal. Since hydrochloric acid was 25% more expensive than sulfuric acid, the latter was selected as more suitable for the acidification of the biodiesel wastewater. Secondly, the pretreated wastewater was treated in the next step by coagulants (aluminum sulfate, polyaluminum chloride or ferric chloride). At the dosage of aluminum sulfate and ferric chloride of 1.0 g/L, the removal of more than 90% and 30% of grease and oil and COD, respectively was achieved without acidification. The optimum dosage of polyaluminum chloride was affected by the pH value. The grease and oil removal of more than 90% could be achieved either at pH of 6–7 and the dosage of 1.0 g/L or at pH 5 and the increased dosage of 2.0 g/L. However, dissolved air floatation, with or without acidification, could not remove grease and oil from the wastewater. Acidification before coagulation with aluminum sulfate reduced the aluminum sulfate concentration by 60–90%, compared to the treatment without acidification. Therefore, dissolved air floatation with acidification and aluminum sulfate coagulation was recommended for treating the wastewater treatment, which yielded the removal of 98–100%, 98.0–99.6%, 80–90% and 80–90% of suspended solids, grease and oil, COD and BOD_5, respectively. Therefore, the pretreatment of the biodiesel wastewater by acidification and coagulation will not only enhance the efficiency of DAF but will also be more economical for the overall biodiesel wastewater treatment process.

3.2. Electrochemical treatments

Compared to conventional processes, this process is interesting for treating industrial wastewaters because of its advantages, such as simple equipment, easy operation, short treatment time, absence or reduced amount of chemicals, fast sedimentation and smaller sludge generation. Electrochemical treatment is performed as electrocoagulation [12,37,38] or hydrothermal electrolysis [39].

3.2.1. Electrocoagulation

In the electrocoagulation process, an electrical current is introduced into the wastewater in an electrochemical cell, usually with an aluminum anode, where the following electrochemical reactions occur [12]:

Anode: $M_{(s)} \rightarrow M(_{aq})^{3+} + 3e^-$

Cathode: $3H_2O + 3e^- \rightarrow 1.5H_{2(g)} + 3OH^-$

Metal and hydroxyl ions, produced at an anode and a cathode, respectively react in an aqueous medium, finally forming amorphous metallic hydroxide flocs with large surfaces:

Solution: $M(aq)^{3+} + 3H_2O \rightarrow M(OH)_{3(s)} + 3H^+$

These flocs enable rapid adsorption of soluble organic compounds and trapping of colloids. The flocs are removed either by sedimentation or floatation by using hydrogen produced at the cathode.

Srirangsan et al. [12] optimized an electrocoagulation process for treating the wastewater generated in a commercial biodiesel production plant with alkali-catalyzed transesterification of frying oil and crude palm oil. A monopolar batch reactor was employed. Five pairs of electrodes, Fe–Fe, Fe–C, Al–Al, Al–C and C–C, were tested. The initial pH, current density and reaction time were varied in the following ranges: 4–9, 3.5–11 mA/cm^2 and 10–40 min, respectively. The optimum conditions for treating the biodiesel wastewater were achieved with a pair of aluminum and graphite electrodes with the current density of 8.32 mA/cm^2 at the initial pH 6 within 25 min. The removal efficiencies for grease and oil, COD and suspended solids were 97.8%, 55.7% and 97.5%, respectively. The process was less effective for removing methanol and glycerol, their removal efficiencies being 16.9% and 3.5%, respectively under the optimum conditions. Compared to the conventional methods, a small amount of sludge was produced, which was easily removed from the processed wastewater. The consumption of aluminum electrode was about 147 mg/L, while the specific energy input was 6.92 kWh/m^3. This study showed that the electrocoagulation process applied might be effective in the primary treatment of biodiesel wastewaters, requiring the secondary treatment for the removal of methanol and glycerol.

Chavalparit and Ongwandee [37] studied the electrocoagulation treatment of the same biodiesel wastewater in the same reactor as those used by Srirangsan et al. [12] and optimized process variables (the initial pH, voltage and reaction time) for removing grease and oils, COD and suspended solids using a method of experimental design. They used a pair of aluminum anode and graphite cathode (Al–C). At the optimum conditions (pH 6.06, voltage 18.2 V and reaction time 23.5 min), grease and oils, COD and suspended solids were reduced by 98.42%, 55.43% and 96.59%, respectively. As it can be concluded from the modest COD removal efficiency, the electrocoagulation process is suitable only for a primary treatment of wastewater derived from the biodiesel production.

To treat a biodiesel wastewater from a base-catalyzed transesterification of cotton oil at laboratory scale, De Meneses et al. [38] applied an electrocoagulation/floatation process. The process was conducted at room temperature in a monopolar batch reactor with a pair of aluminum electrodes, which was equipped with a magnetic stirrer. pH, the reaction time and distance between the electrodes were shown to extremely influence the removal efficiency of the electrocoagulation process. Aluminum ions released during the electrolysis process acted as a coagulant, destabilizing the colloidal system, while the hydrogen gas formed at the cathode promoted floatation. The increase in the pH value of the treated wastewater was observed during the process independently of the initial pH value. Many of the pollutants were separated from the effluent and floated to the surface in the form of sludge. The amount of sludge produced was small and proportional to the current density and the reaction time. The process was very efficient in reducing grease and oil, since its removal efficiency of 99% was achieved. The power consumption was shown to depend on the spacing between the electrodes and the reaction time. From the environmental standpoint, the electrocoagulation/floatation process is a very promising technique which produces the wastewater without apparent color and with almost no grease and oil.

3.2.2. Hydrothermal electrolysis

Hydrothermal electrolysis is a specific electrochemical treatment that converts an industrial wastewater into valuable products using sub-critical water as the reaction medium [39].

When electrolysis is performed in the sub-critical biodiesel wastewater, the water vapor molecules around the anode are ionized or activated and then bombard each other, generating ions, free $OH^{\bullet}$ radicals and sometimes H atoms. In addition, in the liquid phase reaction zone, several liquid water molecules are broken

Table 5
Removal efficiency of electrocoagulation with and without coagulant and oxidant[a]

Parameter	Origin biodiesel wastewater	Removal efficiency, %			
		Electro-coagulation	Electro-coagulation + polyaluminum chloride	Electro-coagulation + hydrogen peroxide	Electro-coagulation + polyaluminum chloride + hydrogen peroxide
Grease and oil, g/L	6.412	83.0	94.0	99.7	100.0
COD, g/L	22.5	47.6	70.0	81.2	94.1

[a] Adapted from Ahmadi et al. [40].

and reform into the gaseous products (hydrogen, hydrogen peroxide and oxygen). Therefore, several oxidants are generated, $OH^{\bullet}$ radicals which is among the strongest ones and can oxidize many stable organic compounds. More details on hydrothermal electrolysis can be found elsewhere [39].

Yuksel et al. [39] investigated the decomposition of a model biodiesel wastewater by the hydrothermal electrolysis using batch and continuous flow reactors. The attention was focused on the effect of process variables (temperature, applied current and electrolysis time) on removing TOC and conversion of glycerol. The model biodiesel wastewater was an aqueous solution of glycerol (0.5 M), methanol (1 M), sodium hydroxide (0.04 M) and oleic acid (2 mM). The reaction pressure and the reaction temperature were 10 MPa and above 200 °C, respectively. Both TOC and glycerol conversions increased with the increase of the applied current. By employing the 1 A current at 250 °C for 90 min, the maximum conversions of glycerol and TOC in the batch reactor were 83% and 23%, respectively. With the flow reactor and by applying the 1 A current at 280 °C within 60 min, the maximum conversions of glycerol and TOC were 75% and 15.9%, respectively.

3.3. Coupled chemical and electrochemical treatment

To improve its efficiency, the electrocoagulation treatment is often combined with a chemical treatment. This combination of chemical and electrochemical treatments can be conducted as one-step [40] or two-step [20,41] process. In the former case, the electrochemical treatment is carried out in the presence of a coagulant and/or an oxidant. In the latter case, the first step of the combined treatment process was acidification of the biodiesel wastewater by adding a mineral acid to recover crude biodiesel, while the electrochemical treatment was carried out in the second step. Usually, even the two-step process cannot reduce the levels contaminants such as grease and oil, COD and BOD below the permitted limits, so a biological post-treatment of the effluent wastewater is needed.

3.3.1. Acidification/electrocoagulation

Ngamlerdpokin et al. [41] developed a two-step process consisted of acidification followed by either chemical coagulation with aluminum sulfate or electrocoagulation. Three mineral acids (sulfuric, nitric and hydrochloric acid) were used to acidify the biodiesel wastewater and to recover crude biodiesel (a mixture of methyl esters and free fatty acids) at different pH values. Higher yields of crude biodiesel were obtained pH 1 and 2.5, but the highest yield was achieved with sulfuric acid. Optimally, about 24.3 mL/L of methyl esters and free fatty acids were removed by sulfuric acid at pH of 2.5 within 7 min. The levels of grease and oil, COD and BOD were reduced for 99.4%, 38.9% and 76.3%, respectively. The aqueous phase from the first step was then treated by chemical coagulation or electrocoagulation processes, which were equally effective, reducing the grease and oil concentration to 105 and 80 mg/L, respectively. Compared to the electrocoagulation, the chemical coagulation produced a better quality of the wastewater with the exception of the BOD level. However, the latter process provided a lower operating cost, compared to the former process.

3.3.2. Electrochemical treatment in the presence of coagulant

Ahmadi et al. [40] studied the removal of grease and oil from the biodiesel wastewater taken from a commercial plant in an electrochemical reactor consisted of four anodes and four cathodes alternated in the electrode pack and equipped with a magnetic stirrer. A gentle agitation was applied to allow the precipitate formed to enlarge and to settle down. In order to compare the process was tested in the absence and presence of polyaluminum chloride as a coagulant and hydrogen peroxide as an oxidant. At pH 7, the increase of current density increased the grease and oil removal, achieving the highest efficiency of 83% at 10 mA/cm^2 within 25 min. Also, with increasing the current density, the energy and electrode (Fe) consumption increased, reaching the maximum values of 0.17 kWh/g and 1.51 g/g of grease and oil. The addition of polyaluminum chloride and hydrogen peroxide affected the grease and oil removal positively, as it can be seen in Table 5. Applying the current density of 10 mA/cm^2 in 25 min at pH 7 and 20 °C, polyaluminum chloride at the concentration of 0.5 g/L reduced the grease and oil content for 94%, while hydrogen peroxide, at the concentration of 2%, caused nearly the complete removal of grease and oil (99.7%). When both polyaluminum chloride and hydrogen peroxide were present in the above mentioned concentrations, grease and oil were completely removed for shorter time (20 min), while the COD removal efficiency was about 94%.

3.3.3. Acidification/electro-oxidation

For the biodiesel wastewater treatment, the electro-oxidation is performed after the acidification of the biodiesel wastewater in order to recover the residual oil, free fatty acids and esters. Electro-oxidation of organic compounds in the aqueous solution does not use any strong oxidizing agents. It is performed through the electrolysis at high anodic potentials in the region of the water discharge, which promotes the generation of weakly adsorbed hydroxyl radicals:

$$S[\ ]+H_2O\rightarrow S[OH^{\bullet}]+H^{+}+e^{-}$$

where S[ ] represents the surface sites for the adsorption of hydroxyl radicals. The formed hydroxyl radicals unselectively and completely mineralize organic pollutants (R) with a high current efficiency:

$$S[OH^{\bullet}]+R\rightarrow S[\ ]+CO_2+H_2O$$

The removal efficiency of electro-oxidation processes is strictly related to operating conditions and selected electrode materials. Boron doped diamond (BDD) [25] and Ti/RuO_2 electrode [20] have been employed in the biodiesel wastewater treatment.

Patiño et al. [25] applied the electrochemical oxidation for treating a biodiesel wastewater produced by a laboratory-scale

base catalyzed transesterification of refined palm oil. Firstly, the original biodiesel wastewater was acidified to recover free fatty acids by subsequent physical methods. Secondly, the processed wastewater was diluted 100 times and then treated by electrochemical oxidation. The investigated factors were current and the sodium chloride concentration, which were tested on four and five levels, respectively. A cell equipped with a boron doped diamond anode and a spiral zirconium cathode, as well as with a magnetic stirrer was used as an electrochemical reactor. The highest removal efficiencies of COD and total organic acid of 58.5% and 61.1% were observed at the current of 0.04 A and the electrolyte concentration of 2.5 g/L, respectively. Under these operating conditions, the removal efficiencies of 9%, 10.4% and 27.5% were achieved for COD, TOC and methanol, respectively and were similar to those observed with the ozonation method.

Jaruwat et al. [20] studied a two-step treatment of the biodiesel wastewater taken from the plant producing biodiesel from the waste cooking oil by a conventional process. In the first step, the concentrated sulfuric acid was added to the biodiesel wastewater which was shaken for 2 h to ensure complete protonation. In this way, the crude biodiesel was recovered (about 6–7%) at a pH of 2–6. Depending on the pH, the levels of grease and oil, COD and BOD were reduced by 87–98%, 40–74% and 13–24%, respectively. In the second step, the aqueous phase was treated by electro-oxidation using a Ti/RuO_2 electrode in the absence or the presence of sodium chloride. The concentrations of grease and oil, COD and BOD were monitored during the electrochemical oxidation, which lasted for 8 h. The effect of current density on the electrochemical oxidation of the pretreated wastewater in the absence of sodium chloride was investigated in the range of 1.84 and 5.51 mA/cm^2 at the initial pH of 2.5. The reduction of the pollutants levels increased with increasing the current density. The application of the current density of 5.51 mA/cm^2 resulted in a complete removal of grease and oil, while the reduction of COD and BOD of 84% and 67%, respectively was achieved within 7 h. These reductions were explained by oxidative degradation of organic pollutants on the anode. The addition of sodium chloride to the electrochemical system promoted a more efficient removal of grease and oil, COD and BOD (20%, 30% and 40%, respectively), compared to that achieved in the absence of sodium chloride. Using the current density of 4.28 mA/cm^2 at the optimum concentration of sodium chloride of 0.061 M, the grease and oil level was completely removed within 2 h, while the levels of COD and BOD were reduced by 90% and 84%, respectively within 5 h. The rate of grease and oil, COD and BOD removal was explained by the kinetics of the pseudo-first order reaction.

3.4. Advanced oxidation technologies

Advanced oxidation processes are nowadays considered as highly efficient physico-chemical processes involving the generation of highly reactive oxidizing species, mainly hydroxyl radicals ($HO^{\bullet}$), able to degrade organic compounds. Among them are ozonation and ozone related processes (O_3/H_2O_2, UV/O_3), heterogeneous (TiO_2/UV) and homogeneous (photo-Fenton process) photocatalysis, etc. Because of hydroxyl radical generation from water electrolysis, electro-oxidation processes can be also considered as advanced oxidation processes. Machulek et al. [44] describe different advanced oxidation processes used for degrading different classes of organic pollutants.

3.4.1. Ozonation

Because of its high instability, ozone is generated onsite, usually by imposing a high voltage alternating current across a dielectric discharge gap through which the air or oxygen passes. Once dissolved into water, ozone undergoes very complex self-decomposition and oxidation reactions. The decomposition reaction forms hydroxyl radicals ($HO^{\bullet}$), strong oxidizing species [44]:

$$2O_3 + 2H_2O \rightarrow 2HO^{\bullet} + O_2 + 2HO_2^{\bullet}$$

Also, ozone molecules can directly react with some organic compounds with high electronic density sites. Because of the low ozone solubility, a liquid phase mass transfer is a rate-controlling step of the overall ozonation process. More information on chemical principles and applications of the ozonation technology in wastewater treatment can be found elsewhere [45].

In addition to electrocoagulation, Patiño et al. [25] applied ozonation as an advanced technology for treating a biodiesel wastewater produced in a laboratory-scale base catalyzed transesterification of the refined palm oil. The wastewater after acidification was diluted and then treated by ozonation at three different ozone flow rates and pH levels at room temperature in accordance with a 3^2 design of experiments with three central points. Preliminary, the study was performed with the 100 times diluted pretreated wastewater. Ozone flow rate was the most significant factor, while pH was not a significant factor. The best ozonation conditions within the evaluation ranges of the factors were ozone flow rate of 0.34 g/h and pH of 12, which resulted in 81.2% and 79.4% removal of COD and TOC, respectively. These best operating conditions were then employed to treat the five times diluted pretreated wastewater. The removal efficiencies for COD and TOC were lower (21% and 22%, respectively) than those obtained for the dilution of 100 times. The removal efficiency for methanol was 31.4%. Finally, the non-diluted wastewater was treated and very low removal efficiencies for COD, TOC and methanol (5%, 12% and 14%, respectively) were observed. The ozonation method was estimated to be a more versatile technology to be applied on a large scale than the electrochemical oxidation.

3.4.2. Heterogeneous photocatalysis

Heterogeneous photocatalysis is defined as the acceleration of photoreaction in the presence of a solid photocatalyst, which can be applied for the purification of the wastewater containing pollutants at low concentrations. The redox processes occurring at the surface of the photocatalyst generate hydroxyl radicals because of the action of UV light and the presence of an oxidizing agent (oxygen from air or hydrogen peroxide). Titanium dioxide is the most widely used photocatalyst to oxidize both organic and inorganic species in wastewaters. UV light is capable of exciting an electron (e^-) from the valence to the conduction band, leaving the hole (h^+) in the valence band [44]:

$$TiO_2 + h\nu \rightarrow e^- + h^+$$

Water can act as an electron donor to the holes of the photocatalyst, generating hydroxyl radicals:

$$h^+ + H_2O \rightarrow HO^{\bullet} + H^+$$

Both holes h^+ and hydroxyl radicals oxidize organic compounds, converting them to carbon dioxide and water. The basic principles, the applications of heterogeneous photocatalysis, as well as the modeling and design of photo-reactors are described elsewhere [46].

Hincapié-Mejía et al. [24] employed heterogeneous photocatalysis with TiO_2 (Degussa P25) immobilized on a silica matrix to treat a biodiesel wastewater from a laboratory alkaline-catalyzed transesterification of the palm oil. A design of experiments involving three factors (pH, hydrogen peroxide concentration and volumetric flow rate) was employed with 100 times diluted biodiesel wastewater. At a hydrogen peroxide flow rate and the

dosage of 0.68 L/min and 1 mL/L, respectively, removal efficiencies of COD and TOC were 60% and 54%, respectively. The removal efficiencies were even lower when the 25 times diluted biodiesel wastewater was treated (3.0% of COD, 1.9% of TOC and 15.3% of methanol), indicating that the heterogeneous photocatalysis is not an appropriate technology.

3.4.3. Photo-Fenton process

The photo-Fenton process (Fe^{2+}/Fe^{3+}, H_2O_2, UV light) oxidizes a wide range of organic and inorganic compounds [44]. In this process, Fe^{2+} ions are oxidized to Fe^{3+} ions by decomposing hydrogen peroxide in the acidic aqueous solution to form hydroxyl radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet}$$

The Fe^{3+} ions, represented by the complex $[Fe(OH)]^{2+}$, are reduced back to Fe^{2+} ions by UV light, producing an additional hydroxyl radical:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+}$$

Hydroxyl radicals are responsible for the degradation of organic compounds by oxidation:

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$$

The photo-Fenton process, which is usually used when a high reduction of COD is required, is one of the most efficient advanced oxidation processes.

In addition to heterogeneous photocatalysis, Hincapié-Mejía et al. [24] studied the photo-Fenton process in a commercial UV reactor applying a design of experiments with two factors: the ferrous ion concentration and the hydrogen peroxide concentration. In this study, 100 times diluted biodiesel wastewater was used. It was observed that UV irradiation drastically increased the removal of COD, while in the absence of UV irradiation (the Fenton reaction) a small COD removal was achieved. The COD removal was better in the presence of iron at concentrations of 0.1 mM and 0.3 mM, while the latter was the optimum for the TOC removal. The optimum hydrogen peroxide concentration for COD and TOC removal was 35 mM. When five times diluted biodiesel wastewater was treated by the photo-Fenton at iron and hydrogen peroxide concentrations of 0.3 mM and 35 mM, respectively, the removal efficiencies of COD, TOC and methanol were 80.3%, 85.7% and 99.5%, respectively. However, much lower removal efficiencies were achieved for all three pollutants (7.0% of COD, 27.2% of TOC and 23.8% of methanol) when the original biodiesel wastewater was treated by the photo-Fenton under optimum conditions. This method could be suitable at a large scale after the physico-chemical pretreatment of the biodiesel wastewater.

3.5. Biological treatment

Biodiesel wastewaters are characterized by high COD levels (in the range of 18–590 g/L), as it can be seen in Table 1. Considering the high content of biodegradable organic compounds, biodiesel wastewaters seem to be a very promising raw material for microbial degradation. However, a biological treatment of the wastewater from biodiesel plants is difficult because its composition is not suitable for microbial growth. The wastewater has a high pH value and is poor in nutrients needed for microbial growth, except for the carbon source (residual oil, methanol and glycerol), so minimum amounts of important nutrients should be added. Methanol is a good substrate for microorganisms. Its high concentration in biodiesel wastewaters favors the fast microbial growth [23]. This can be useful in a biological treatment of the biodiesel wastewaters containing slowly degradable residual oil. However, a too high methanol concentration is toxic to methanogens [47], and too high residual oil content can inhibit the microbial growth in the biological treatment. Free fatty acids are reported to inhibit the anaerobic digestion process [48]. Also, high salinity of the biodiesel wastewater can negatively influence some microorganisms, such as methanogens. Therefore, a biological treatment of biodiesel wastewaters should be undertaken under optimum operating conditions, including biodegradation of the residual oil. However, a biological treatment of biodiesel wastewaters such as for biogas generation has not been sufficiently investigated yet.

Suehara et al. [11] developed a biological treatment system with the control of temperature useful for small-scale biodiesel production plants. In this study, the biodiesel wastewater was obtained from a plant employing the alkaline-catalyzed transesterification. This wastewater had high levels of pH, oil and dissolved solids, but the low nitrogen concentration. Therefore, small amounts of the nitrogen source (ammonium sulfate, ammonium chloride or urea), yeast extract, potassium dihydrogen phosphate and magnesium sulfate were added to the wastewater to avoid eutrophication. They used *Rhodotorula mucilaginosa*, the oil degradable yeast, and enriched the biodiesel wastewater. The pH was adjusted at 6.8. When urea was the nitrogen source, the optimal carbon-to-nitrogen ratio was in the range of 17–68. The initial yeast extract concentration of 1 g/L was optimal. A growth inhibitor was detected in the wastewater, and the working microorganism could not grow if the solid content was higher than 2.14 g/L. The growth inhibition was avoided by diluting the wastewater with the same volume of water. The oil degradation was fast in the diluted wastewater under the optimal conditions, when the removal efficiency of 98% was achieved. This biological treatment system was recommended as suitable for small-scale biodiesel production plants [11].

Kato et al. [42] used a continuous consortium bioreactor for the treatment of the biodiesel wastewater with the oil and grease concentration of 120 g/L. The reactor contained a bacteria-fixed ceramic material having the capability of the high-oil degradation. The most important bacteria of the consortium system were *Acinetobacter*, *Bacillus* and *Pseudomonas*. The optimal operating conditions were determined by batch tests: pH 6, 30 °C and air agitation. The reactor operated almost maintenance-free for 1 year. Grease and oil levels were nearly completely removed from the biodiesel waste water, the final grease and oil concentration in the treated waste water being 10–30 mg/L.

Da Rocha et al. [49] isolated and tested the microorganisms with high potential of the lipase production from the biodiesel wastewater of an industrial plant for transesterification of the soybean oil with methanol in the presence of sodium methoxide. The biodiesel wastewater contained 6.76 g/L of grease and oil. One of the microorganisms, identified as *Klebsiella oxytoca*, removed 80% of grease and oil from the biodiesel wastewater in 48 h.

3.6. Coupled physico-chemical, electrochemical, advanced oxidation and biological processes

Both anaerobic and aerobic processes can be used for a biological treatment of the biodiesel wastewater, depending on the COD value of the raw wastewater. The anaerobic process is used in the case of high values of influent COD ($>$100,000 mg/L) [23,43,50], while the aerobic process was applied for treating the biodiesel wastewater with the COD value smaller than 100,000 mg/L [27]. The raw biodiesel wastewater is first acidified to remove the residual oil, free fatty acids and esters. In some cases, the effluent wastewater was further treated prior to the biological process, by coagulation/sedimentation [23], coagulation/flocculation [43], or electrocoagulation/floatation [43,50]. The photo-Fenton process was also coupled with the aerobic process [26].

3.6.1. Physico-chemical/anaerobic processes

Phukingngam et al. [23] treated the biodiesel wastewater from a small-scale commercial plant for the biodiesel production combining a physico-chemical pretreatment and an anaerobic baffled reactor (ABR) to reduce the organic load and to produce biogas. The biodiesel wastewater had high methanol and COD contents of 40.3 and 56.4 g/L, respectively. It also contained the residual oil (greases and oil of 3.3 g/L), glycerol (2.4 g/L), soap and suspended solids (0.4 g/L). However, a very low nitrogen content of 14 mg/L was found, while the phosphorus content was not detected. Because of a high grease and oil content, the biodiesel wastewater was pretreated by acidification, chemical coagulation and sedimentation. The pH value of the biodiesel wastewater was first adjusted to 4 by sulfuric acid. Then, polyaluminum chloride (62.5 mg/L) and a cation polymer as a coagulating aid (1.25 mg/L) were added. The pretreatment resulted in 96% removal efficiency of grease and oil. However, the COD value was reduced only for 22%. Therefore, the biological treatment in ABR was applied in order to increase the efficiency of the overall process. After the addition of urea, K_2HPO_4 and $FeCl_2$ to the pretreated wastewater it was diluted with the tap water to a predetermined COD concentration. The influent flow rate of 2.2 L/d and the hydraulic retention time of 10 days were held constant. When the ABR operated at 1.5 kg/m^{3}d of COD, the best COD, methanol and glycerol removal efficiencies of 99%, 100% and 100% respectively were achieved. The COD removal was gradually reduced longitudinally, being the highest in the first compartment of the ABR.

Siles et al. [43] evaluated the effect of two pretreatments of the wastewater from the biodiesel production over a mesophilic anaerobic digestion. Firstly, in a pretreatment step, the wastewater was acidified by sulfuric acid until to a final pH value of less than 4 to recover about 3.8% of the waste containing free fatty acids. This waste was recirculated in the biodiesel production process. Then, the aqueous phase was separated from the waste by centrifugation, neutralized and subjected to electrocoagulation/floatation or coagulation/flocculation at laboratory scale. The former process was performed at pH of 8.07 and the latter was conducted at pH of 9.26. A continuous stirred tank reactor and a batch stirred tank reactor were employed for the two processes, respectively. The electrochemical reactor had eight aluminum electrodes to which a direct current (1.5 A, 12 V) was applied within 30 min. In the coagulation/flocculation process, aluminum polychloride and Actipol A-401 were used as a coagulant and a flocculant, respectively. The coagulant was added to the wastewater which was vigorously stirred for 2 min. Then, the flocculant was added and the mixture was gently stirred for 1 min. After standing for 20 min, the float and the precipitate were removed from the aqueous phase. COD removal efficiencies of 45% and 63% were observed for the electrocoagulation/floatation and the coagulation/flocculation, respectively. Finally, both pretreated wastewaters were subjected to anaerobic digestion in the bioreactors initially inoculated with methanogenically active granular sludge (12 g/L of volatile suspended solids) at 37 °C. The bioreactors were magnetically stirred. The biomethanization of the electrocoagulated and coagulated wastewaters yielded a COD removal of 99% and 94%, respectively. The methane yield coefficient was similar for both processes (about 297 mL CH_4/g COD removed). However, the allowed organic loading rate and the average methane production rate were considerably higher for the acidified and electrocoagulated wastewater. The authors concluded that the combination of anaerobic digestion coupled with electrocoagulation might be suitable for the efficient purification of biodiesel wastewaters.

Siles et al. [50] performed the co-digestion of the wastewater generated from the biodiesel production from the waste cooking oil at 35 °C. At first, the wastewater was acidified with sulfuric acid (final pH less than 4) and centrifuged to separate the oil/biodiesel phase. The aqueous phase was neutralized by sodium hydroxide and subjected to electrocoagulation/floatation to reduce the oil content. After 30 min of electrocoagulation, total and soluble COD decreased by 6.25% and 13.06%, respectively. However, the decrease of total COD by the overall process (acidification, centrifugation and electrocoagulation) was 45%. The resulting aqueous phase was mixed with glycerol at a proportion of 85:15 (COD). Finally, the anaerobic process involving the mixture of glycerol and the processed wastewater and methanogenically active granular sludge as inoculum was performed in a batch laboratory-scale reactor, reaching the biodegradability of around 100%. The inoculum was obtained from an anaerobic reactor used for treating brewery wastewater.

3.6.2. Physico-chemical/aerobic processes

De Gisi et al. [27] performed a full-scale treatment of the wastewater derived from a biodiesel production plant with alkali-catalyzed transesterification, which included several stages such as primary (neutralization, adsorption, coagulation, flocculation and sedimentation), biological (combined trickling filter and activated sludge system), secondary (coagulation, flocculation and sedimentation) and reverse osmosis processes. All the processes were continuous, except for the reverse osmosis system. The upstream physico-chemical pretreatment is useful in removing lipophilic compounds (methyl esters, free fatty acids, unreacted acylglycerols), which inhibit the subsequent biological process. Because of a high organic load, pure oxygen is worth using in the biological process. The secondary physico-chemical process is used to prevent the de-flocculation of the activated sludge and to increase the sludge sedimentation. The COD removal from the wastewaters tested by the continuous process was more than 90%. After the secondary sedimentation, the aqueous phase was treated with sand filters, followed by reverse osmosis to remove biorefractory COD and salts. The reverse osmosis system consisting of spiral membranes was employed with the rejections of 92.8%, 95.0% and 99.5% of soluble COD, chlorides and sulfates, respectively.

3.6.3. Photo-Fenton/aerobic process

Ramírez et al. [26] used a coupled system of the photo-Fenton and an aerobic sequential batch reactor to treat a biodiesel wastewater derived from an alkali-catalyzed transesterification process using palm or castor oils. The individual treatment processes were also evaluated. The photo-Fenton was conducted in a commercial UV reactor. After adjusting the pH to 2.3, a solution of hydrogen peroxide (35 mM) and ferrous sulfate (0.3 mM) was added to the biodiesel wastewater. The aerobic sequential batch reactor with a biodiesel wastewater was loaded with sludge as an inoculum. A solution of nutrients was also added to the reactor for the biomass acclimatization under aerobic conditions. After the acclimatization, the nutrient solution was removed, and the reactor was refilled with the biodiesel wastewater. Both processes were effective at purifying the biodiesel wastewaters, but, compared to the coupled system, they required longer reaction times. For the palm oil biodiesel wastewater, the coupled system contributed to a significant removal of COD and BOD ($>90\%$) as well as TOC (72%). The removal efficiencies for the castor oil biodiesel wastewater were lower (76.1%, 69% and 67.7% form COD, BOD and TOC, respectively). The coupled process system required only 7 days, which was half of the time required for the biological process itself.

Table 6
Advantages, disadvantages and possibilities for improvement of biodiesel wastewater treatment processes.

	Advantages	Disadvantages	Possibilities for improvement
Physico-chemical treatments			
Adsorption	Simple process design	Multistage treatment is needed for obtaining satisfactory water quality	Selection of efficient and reusable adsorbent with selective affinity
	Effective in separating a wide range of chemical compounds	Increase of costs with each additional stage	Use of low-cost adsorbents based on natural materials, agricultural wastes and industrial wastes
	No sludge is produced	Need to regenerate spent adsorbents	Use of column-type continuous-flow operation, especially expanded-bed adsorber
	Additional reagents to overcome high alkalinity are not needed	Requires separation of used adsorbent in batch operations	Optimization of process conditions
	pH of treated wastewater is unaffected	Requires regeneration of used adsorbent in continuous-flow operation	
	High degree of stability and reliability	Disposal of spent adsorbent	
	Flexibility in design and operation		
	Low investment in term of initial cost and land required		
Coagulation/ flocculation	Relatively simple process design	Multi-step process	Use of more efficient coagulants, especially natural materials, that are biodegradable
	Relatively short duration time	Large treatment area	Coupling of acidification and coagulation for efficient removing of COD and grease and oils
	Effective in the removal of grease and oil	Ineffective in COD removal	Optimization of process conditions
	Use of low-cost inorganic salts as coagulant	Contamination of treated wastewater by chemical coagulants	
	Cost effective process with low operating and capital costs	Optimum treatment conditions should be determined experimentally for each batch of biodiesel wastewater	
	Can be automated	Can require further treatment of processed water	
		Sludge formation that is classified as hazardous waste	
		Requires secured land-filling of hazardous solid wastes	
Dissolved air floatation	Easy to install and operate	Multi-step process	Application of recycle pressurization
	Rapid startup	Large treatment area	Improvement of air-dissolved flotation design
	Can deal with high operation rate	Time consuming process	Optimization of process conditions
	Thicker sludge production	Requires pretreatment of wastewater by acidification and coagulation	
	Flexibility in changing operation parameters	Requires further treatment of processed water	
	Highly efficient for removing suspended grease and oil, solid, turbidity and color	Increased operating and maintenance costs	
Electrochemical treatments			
Electro-coagulation process	Simple and easy to operate and maintain	Modest efficiency of COD removal	Development of advanced and less-cost electrode materials
	No added chemicals	Regularly replacement of electrodes	Application of different types of electrodes
	Able to fulfill simultaneous coagulation and flotation	Requires pretreatment of wastewater by acidification	Increase of current efficiency
	Fast rate of pollutant removal	Requires further treatment of processed water for removing methanol and glycerol	Optimal design for electrolytic reactors
	Efficient in reducing grease and oil	High electricity costs	Addition of coagulant aid or oxidant
	Effective in destabilizing fine colloidal particles	High investment costs	Optimization of process conditions
	Low sludge production		
	Fast sedimentation		
	Non-hazardous reaction products		
	Small sludge generation which is easily removed		
	Easy process automation by adjusting current		
Hydrothermal electrolysis	Electric current at hydrothermal conditions enhances degradation (oxidation) reactions	Modest efficiency of glycerol and total organic carbon removal	Experimentation with real biodiesel wastewaters
	Use of sub-critical water as reaction medium without any solvent or catalyst	Additional treatment is needed for removing residual organic matters	Electrochemical degradation pathway should be clarified
	The controlled generation of oxygen, so there is no need for additional oxidizer	High electricity costs	Optimization of process conditions
	Energy consumption for electrolysis is minimized	High investment costs	

Table 6 (*continued*)

	Advantages	Disadvantages	Possibilities for improvement
	Generation of highly reactive hydroxyl radicals		
	Conversion of pollutants into various compounds		
	Decomposition of some stable components, such as glycerol		
	Short treatment time		
Electro-oxidation process	Simple and easy to operate and maintain	Low removal efficiencies for COD, TOC and methanol	Development of advanced and less-cost electrode materials
	No added chemicals	Raw biodiesel wastewater should be diluted	Increase of current efficiency
	Efficient removal of COD, BOD and grease and oil	Addition of electrolyte to enhance removal of pollutant	Optimal reactor design
	Efficient degradation of organic pollutants	Requires pretreatment of wastewater by acidification	Combination with other treatment methods
	Short reaction time	Regularly replacement of electrodes	Optimization of process conditions
	Easy process automation by adjusting current	High electricity costs	
		High investment costs	
Advanced oxidation technologies			
Ozonation process	High reactivity of ozone	Low removal efficiencies for COD, TOC and methanol	Further experimentation with ozone treatment of biodiesel wastewater is needed
	Eliminates odors	Raw biodiesel wastewater should be diluted	Development of new ozone contacting devices that will be compatible with more energy-efficient, high-concentration ozone generators
	Reduces COD, color and surfactants	High capital cost and electric consumption	
	Removes solids by oxidation and physical floatation	Highly corrosive system, thus requiring corrosion-resistant material	
	No harmful residuals that need to be removed	Cannot remove dissolved minerals and salts	
	Fewer safety problems associated with shipping and handling	Not economical for high levels of suspended solids, BOD and COD	
	Elevates dissolved oxygen concentration	No measurable residual to indicate removal efficacy	
		Remaining ozone must be destroyed before release into atmosphere	
Heterogeneous photocatalysis	Degradation of pollutants under ambient conditions	Low removal efficiencies for COD, TOC and methanol	Further experimentation with biodiesel wastewater treatment by heterogeneous catalysis is needed
	Excellent removal efficiency for many organic and inorganic pollutants	Raw biodiesel wastewater should be diluted	Development and use of more efficient photocatalyst
	Treats effluents containing a wide range of concentrations ofpollutants	Limited penetration depth of incident radiation into TiO_2 suspensions because of strong light scattering	
	Relatively low cost of TiO_2	Batch reactors require additional unit operations to separate catalyst from solution	
	Biological and chemical inertness of TiO_2 and insolubility in water	Generation of catalyst sludges	
	Possibility of TiO_2 immobilazation	Physico-chemical pretreatment is needed	
	Solar radiation can be used for activating TiO_2		
Photo-Fenton process	Organic pollutant destruction	Low removal efficiencies for COD, TOC and methanol	Further experimentation is needed
	Biodegradability improvement	Raw biodiesel wastewater should be diluted	Development of new catalysts that function at neutral pH and do not require removal the end of the process
	Removal of COD, BOD, odor and color	Requires addition of iron salt	
	Produces oxidation products of low toxicity	High costs	
	Offers the possibility of using solar radiation as the source of light	Requires the low pH	
	Spontaneous decomposition of residual hydrogen peroxide into water and oxygen	Physical-chemical pretreatment is needed	
	No energy input is necessary to activate hydrogen peroxide	Iron catalyst should be removed after the process by increasing the pH	
		Production of a substantial amount of $Fe(OH)_3$ precipitate	
Biological treatment			
General consideration	Suitable for treating wastewaters with high organic content	The presence of microbial growth inhibitor(s) biodiesel wastewaters	Optimization of process conditions
	Simple process with no need of controllers, except for a temperature	Pretreatment of biodiesel wastewater is needed because of high pH value and residual fatty acid esters	

Table 6 (*continued*)

	Advantages	Disadvantages	Possibilities for improvement
	Efficient removal of pollutants	Important nutrients for microbial growth should be added	
	Mild operational conditions		
	Economically favorable, both in terms of capital investment and operating costs		
Anaerobic process	Production of biogas (almost 90% conversion of potential energy in carbon)	May produce odor	Optimal reactor design
	Production of polyhydroxyalkanoates production	Long start-up periods	Optimization of pretreatment process (acidification, coagulation, electrocoagulation)
	Production of small amount of biomass that reduces sludge disposal costs	Time consuming process	
	Low energy requirement	Slightly higher organic content in effluent, compared to aerobiaclly treated wastewater	
	Small area requirement		
	Low requirements for nutrient dosage		
Aerobic process	Flexible process	Production of large amount of sludge that increases sludge disposal costs	Optimization of upstream and downstream physico-chemical treatments to improve pollutant removal efficiency
	Short reaction time	Requires extensive land area for treatment	Application of the photo-Fenton process as a pretreatment stage to improve the efficiency of the overall treatment process
		Higher costs for nutrient dosing	
		High energy requirements for aeration	

4. Comparison of various biodiesel wastewater treatments

Real biodiesel wastewaters derived from laboratory or commercial scale processes of alkali-catalyzed transesterification using methanol have been studied so far, although the models of the biodiesel wastewater have been used in a couple of studies. The origins and characteristics of biodiesel wastewaters, treatments applied and removal efficiencies of certain contaminants are reviewed in Table 2. Different vegetable (palm oil, castor oil) and waste cooking oils are used as oily feedstocks. The use of only sodium or potassium hydroxide as a catalyst has been reported. Probably, the transesterification process conditions (methanol-to-oil ratio, catalyst loading and reaction temperature) and the production plant capacity vary from case to case. Different procedures for water washing crude biodiesel are applied. Therefore, it is obvious that both volume and chemical composition of the biodiesel wastewater produced vary in different processes of crude biodiesel washing, which results in different type and load of the output pollution. Most frequently, the levels of COD, BOD, grease and oil, TOC, total suspended solids, methanol and glycerol are monitored before and after the biodiesel wastewater treatment. Also, different operating conditions are applied in different treatment processes, such as different type and dosage of coagulant in physico-chemical processes, type of electrodes and current densities in electrochemical processes, etc. In some cases, different pretreatments of the biodiesel wastewaters are conducted.

4.1. Advantages, disadvantages and possibilities for the improvement of biodiesel wastewater treatments

Biodiesel wastewater treatment processes have considerable advantages and disadvantages in practical applications, as it can be seen in Table 6, which should be carefully analyzed when selecting the most suitable treatment method. Based on comparing these inherent advantages and limitations, future research activities are also highlighted in Table 6.

4.2. Comparison of the biodiesel wastewater treatment efficiency

Since different input biodiesel wastewaters are employed in different studies, it is difficult to compare different treatments with respect to their contaminant removal efficiencies. However, some generalizations can be drawn based on the removal efficiencies (Table 2), advantages and disadvantages of individual biodiesel wastewater treatments (Table 6).

Proper acidification and chemical coagulation/flocculation successfully remove grease and oil but they are unsuccessful in removing COD. Aluminum sulfate, polyaluminum chloride and ferric chloride are equally effective for the removal of residual oil and COD. In addition, coupled acidification and chemical coagulation is efficient in removing both pollutants. The application of air floatation improves this chemical treatment by removing total suspended solids. The electrochemical treatment is characterized by the same efficiency as the chemical one. The combinations of chemical methods (acidification, coagulation) with the electrochemical treatment improve the removal efficiencies of COD and BOD, compared to both individual treatment processes. The optimum treatment conditions, such as dosages of acid, coagulant, flocculant, current density, reaction time etc., should be probably determined experimentally for each batch of the biodiesel wastewater.

Advanced oxidation technologies appear not to be effective in removing the contaminants (measured through COD) from raw biodiesel wastewaters. It is observed that their removal efficiency increases with diluting the raw biodiesel wastewater. Further optimization studies are needed to achieve an acceptable removal of contaminants. It can be expected that a pretreatment process, such as a physico-chemical one, will probably increase their removal efficiency. Among the so far employed advanced oxidation technologies, the photo-Fenton process seems to be the most promising one. The process can be also used as a pretreatment for the subsequent biological treatment. A number of significant challenges must be overcome to make advanced oxidation processes generally applicable for treating biodiesel wastewaters.

The individual biological treatment is demonstrated to be inefficient in treating a raw biodiesel wastewater because of the presence of microbial growth inhibitor(s). The pretreatment of the biodiesel wastewater with acidification, chemical coagulation, electrocoagulation or photo-Fenton improve the performance of biological processes. Considering the high content of readily degradable organic substances, the biodiesel wastewater is a promising raw material for anaerobic degradation with biogas as a product. However, the possibility of biogas generation has not been enough studied yet. Chavalparit and Raghareutai [51] reported the production of biogas containing 74.5% methane from the biodiesel wastewater on a laboratory scale in an anaerobic baffled reactor with the hydraulic retention time of 10 days and the capacity of 0.38 m^3/kg COD.

4.3. Economic aspects of the biodiesel wastewater treatment

The simplest management of the biodiesel wastewater is sending it to a treatment plant of the wastewater agency [22]. However, the biodiesel wastewater must pass the quality standards of the treatment plant. Therefore, the common procedure is to treat the biodiesel wastewater in a pretreatment system prior to a delivery to the treatment facility. This is probably the most costly way of the biodiesel wastewater management since the biodiesel factory has to pay around 128.45–160 US$/$m^3$.

In the past, the biodiesel factories have tried to handle their biodiesel wastewaters by composting or incinerating in cement industry. Composting is likely to be cheaper than many other discharge methods but it may lead to insignificant cost savings (15.85 US$/$m^3$–132.09 US$/m^3) [52]. Incineration of the biodiesel wastewater in the cement industry reduces the biodiesel wastewater management costs to around 60 US$/$m^3$ [22,41].

The application of a chemical treatment is based on using chemicals, which influences the process economy. Therefore, the selection of chemicals should be based on the cost of both coagulant and mineral acid used in the chemical treatment. For example, the costs for the treatment with hydrochloric and sulfuric acid are about 0.09–0.13 US$/$m^3$ and 0.38–0.51 US$/$m^3$, respectively while the treatments using ferric chloride or ferric chloride plus a polymer and a reagent for the pH adjustment are 0.52–0.71 US$/$m^3$ and 1.47–1.66 US$/$m^3$, respectively [35]. The total expenses of the biodiesel wastewater treatments using aluminum sulfate and polyaluminum chloride that include the chemical and labor costs were 3.14 US$/$m^3$ and 3.36 US$/$m^3$, respectively [22]. Also, it is reported that aluminum sulfate is cheaper than polyaluminum chloride and ferric chloride by 10% [21,36] and 263% [21], respectively. In addition, a low amount of sludge is generated when using aluminum sulfate, reducing the cost of the sludge disposal. For a biodiesel production plant with the daily capacity of 100,000 L of biodiesel, the cost of the biodiesel wastewater treatment with chemical coagulation agents does not reach 0.7% the annual turnover of the company [10,34].

The pretreatment of the biodiesel wastewater by acidification and coagulation/flocculation enhances the efficiency of dissolved air flotation. It is claimed that the operating cost of the combined treatment process is lower than using the chemical treatment only [21].

Besides their costs, the other possible benefits of using a chemical agent should be also considered. For instance, sulfuric acid is a more suitable acid for the biodiesel wastewater acidification than other mineral acids since it provides the most effective recovery of organic substances (particularly of biodiesel and grease and oil), influencing the overall biodiesel production process economics positively [21].The saving cost, obtained from the cost of recovered methyl esters, is greater than the cost of sulfuric acid by around 0.29 US$/$m^3$ [22]. The additional advantages of acidification are as follows: the properties of the recovered methyl esters are in the range of the majority biodiesel quality standards and the recovered oil can be used back in the biodiesel production [21]. Sulfuric acid is also less harmful to activated sludge systems than hydrochloric acid [21], which is important if the processed wastewater is further biologically treated. However, even using sulfuric acid for acidification the COD level remains high, so the processed wastewater requires further treatment prior to discharge [21], such as biological treatment in sedimentation ponds.

Typical costs of the wastewater treatment with the electrochemical process are the expenditure on the energy consumption, the mass loss of electrodes and the electrode materials [37]. The overall costs are yielded by a pretreatment process involving acidification. The electrocoagulation process (1.74 US$/$m^3$) has a greater operating cost than the pure chemical coagulation process (1.07 US$/$m^3$) [41].

There is no data on the costs of biological wastewater treatment processes in the available literature. The biological processes are considered to be an economical way for reducing the environmental impacts of biodiesel wastewaters [33]. Generally, the capital cost for anaerobic digesters is of the order of 144,000 US $/t of COD treated per day [53]. However, the costs of anaerobic digestion can be reduced through the utilization of the biogas for heat or the electricity energy generation.

5. Other uses of biodiesel wastewater

Besides the treatment methods, there are some attempts to utilize the biodiesel wastewater and crude glycerol for the biogas production [23,50], for the polyhydroxyalkanoates (PHAs) production by a mixed microbial consortium [54], as a substrate for the denitrification phase of the biological treatment of nitrogen-rich wastewaters in a sequential batch reactor [14], for growing algae in photo-bioreactors [55] and electricity generation in bio-filter circuit systems [56,57]. If the biodiesel wastewater does not contain methanol, it can be used without any purification for farm irrigation [58].

Phukingngam et al. [23] used the processed biodiesel wastewater from a chemical treatment for the biogas production in an anaerobic baffled reactor (ABR). Urea, K_2HPO_4 and $FeCl_2$ were added to the pretreated wastewater to achieve the COD:N:P:Fe ratio of 150:1.1:0.2:0.33. Prior to feeding the ABR, the enriched pretreated wastewater was diluted with tap water to a desired COD concentration. The seed sludge for the ABR, taken from a wastewater treatment plant, was acclimated to the diluted wastewater for 2 months. The hydraulic retention time of 10 days and the influent flow rate of 2.2 L/d were maintained constant. With increasing the organic loading rate from 0.5 kg/m^3d to 1.5 kg/m^3d of COD the production rate of biogas increased from 2.1 L/d to 12.4 L/d. The further increase in organic loading rate did not influence the biogas production rate. Under the optimal value of the organic loading rate (1.5 kg/m^3d of COD), the methane content in the obtained biogas was 64–74%. At organic loading rates higher than the optimum one, the utilization of the substrate was decelerated because of the excessive accumulation of volatile fatty acids causing the reduction of pH, which was unfavorable for methanogenesis.

In the work of Siles et al. [50], methane was produced by the anaerobic co-digestion of a mixture of glycerol and the wastewater from the biodiesel production process. This mixture replaces the clean water needed to dilute glycerol and nutrient requirements. Revalorizing both wastes, the process is not only environmentally but also economically beneficial. Prior to the anaerobic co-digestion, glycerol was acidified with phosphoric acid to neutralize the catalyst, while the wastewater was acidified with sulfuric acid (pH less than 4), neutralized by sodium hydroxide and subjected

to electrocoagulation. Thereafter, the anaerobic process involving methanogenically active granular sludge was performed, permitting the biodegradability of around 100% and the methane yield of 310 mL CH_4/g COD removed. The methane production rate was constant at 0.63 mL CH_4/(g VSS g COD h) in the applied range of organic loading rate.

Coats et al. [54] studied the PHAs production and cocurrent COD removal in shaken flasks at 30 °C for 4 days, utilizing biodiesel wastewaters with and without residual ethanol and a PHA-producing microbial seed. Surprisingly, the PHA yield was 6% and 10% on the wastewaters with and without ethanol, respectively, since ethanol is a direct precursor for PHA synthesis. Also, COD reduction was 60% and 67% in the absence and presence of ethanol in the biodiesel wastewater, respectively.

Malá and Malý [14] used the wastewater from a commercial plant with base-catalyzed transesterification having high COD (300–500 g/L) and methanol (6–10% by vol.) as a carbon substrate for denitrification of the nitrogen-rich sludge liquor from anaerobic sludge digestion in a sequential batch reactor. The maximum rate of denitrification was 9.1 mg/g h, and the concentration of nitrogen (NH_4) in the effluent was less than 10 mg/L. The COD dosage of 3.5–4.5 g/g of nitrogen was found to be optimum for denitrification. The reactor operated steadily at the hydraulic retention time of 4–5 days.

Lamers [55] reported the feasibility of using biodiesel wastewater to which some nutrients (corn powder hydrolysate as a glucose source and commercial COMBO media as a trace elements supplement) were added for growing alga *Chlorella protothecoides* in photo-bioreactors. This alga showed an excellent ability to remediate the biodiesel wastewater by converting glycerol, methanol and catalyst into the biomass or other organics. After the algae harvesting, the residual water contained small amounts of unharvested biomass and unused substrates, which were successfully removed by the diatomaceous earth filtration. The algal lipids are viable for the biodiesel production and the remediated water can be reused.

Sukkasem et al. [56] developed an upflow bio-filter circuit system (UBFC) consisting of pre-fermentation, influent adjustment, up-flow anaerobic filter and bio-filter circuit for electricity generation from the biodiesel wastewater. The biodiesel wastewater is treated in the UBFC system without the chemical pretreatment or nutrient addition. Because of the use of granular activated carbon electrodes, the problem of bio-particle clogging in the UBFC during operation occurred. To solve this problem Sukkasem and Laehlah [57] substituted granular activated carbon by the carbon fiber brush. Bio-electrodes were prepared by inoculation in the activated sludge for 3 days to immobilize the microorganisms on the electrode surface as a biocatalyst producer. The process started by feeding 6.0 g COD/L of the wastewater influent into the UBFC at 1.0 mL/min. The cathode was aerated at 2.0 L/min to stimulate the growth of aerobic microorganisms on the bio-electrode surface. The UBFC system was operated until the output voltage stabilized at >0.6 V in an open circuit mode. Before fermentation, the wastewater was inoculated by the activated sludge (20% v/v) in order to increase the fermentation rate. The supernatant of the fermented wastewater was adjusted to the 30.0 g/L COD concentration and neutralized before being fed into the UBFC after the circuit connection. The biodiesel wastewater fed into the UBFC system under the following optimal conditions: organic loading rate of 30.0 g COD/(Ld), hydraulic retention time of 1.04 days and aeration at 2.0 L/min. The highest efficiency of COD removal (67%; 20.1 g COD/Ld) was achieved at the exterior resistance of 10 kΩ. The bio-filter circuit generated quite low electricity (35.62 mW/m^3 of anode volume), which was attributed to a large internal resistance caused by a low degree of biodegradation, a long distance between electrodes or material sensitivity. Therefore, further improvement of these operational factors was recommended. A further development of UBFC system should be also focused towards the improvement of the system construction and the optimization of the pre-fermentation step in order to achieve the higher power generation and the scale-up of the system.

The reuse of the pretreated wastewater is also an interesting alternative. For this purpose, the wastewater from the biological treatment should be subjected to a secondary chemical sedimentation, filtration and reverse osmosis. Myint et al. [59] included a single stage reverse osmosis system into a process plant producing biodiesel from soybean. Their computer-aided simulations using ASPEN Plus showed that the savings obtained including water recycling from reverse osmosis system can be up to 24,000 US$ /year. According to this calculation, about 41% of discharged wastewater could be recycled, while the remaining amount should be sent to the wastewater treatment.

Glycerol, a by-product of the biodiesel production process, diluted with tap water, is frequently used for the biogas production in anaerobic sequencing batch reactors [60,61] and anaerobic sequencing batch biofilm reactors [62,63]. Also, Ito et al. [64] optimized the use of crude glycerol from the biodiesel industrial process after dilution with deionized water and nutrient supplements (yeast extract and tryptone) for hydrogen and ethanol synthesis by *Enterobacter aerogenes*. Siles et al. [50] have already investigated the anaerobic co-digestion of the mixture of glycerol and untreated biodiesel wastewater in batch laboratory-scale reactors. Therefore, future use of the biodiesel wastewater could be aimed at the production of valuable products (methane, hydrogen, ethanol, lipids, etc.) from crude glycerol diluted with untreated or treated biodiesel wastewater.

6. Swot analysis of biodiesel wastewater treatment

The SWOT analysis is applied to identify the feasibility of the biodiesel wastewater treatment, which is focused on both current (strengths and weaknesses) and future (opportunities and threats) conditions. The results of the SWOT analysis are summarized in Table 7. The positive trend for treating the biodiesel wastewater is observed. The necessity for future studies on the feasibility of the biodiesel wastewater treatment is confirmed. The focus should be on the minimization of the wastewater generation and the reduction of pollutant levels by introducing more suitable biodiesel production processes, the modification of traditional biodiesel production processes, the combination of various treatment methods, the development of more efficient and less-cost treatment methods, the improvement of the existing and novel treatment processes and the implementation of new uses of the biodiesel wastewater.

7. Future perspectives for the biodiesel wastewater treatment

The biodiesel industry tends to reduce the amount of the biodiesel wastewater as much as possible, aiming at a zero discharge process. Thus, perspectives for the biodiesel wastewater treatment include all methods which result in the reduction of the biodiesel wastewater quantity and/or concentrations of carbonaceous compounds, resulting in reusable process water. Different approaches can be applied to achieve the reduction or even elimination of the biodiesel wastewater such as the improvement of transesterification reaction, the use of novel purification methods, the modification of crude biodiesel purification stage, and the development of the efficient wastewater treatment process leading to clean and reusable water. The first two approaches are

Table 7
SWOT analysis of biodiesel wastewater.

Positive **Strengths**	Negative **Weaknesses**
Water washing is very often more suitable method for purification of crude biodiesel than other methods.	Generation of large biodiesel wastewater amount (from 20 to 300 L per 100 L of biodiesel produced), which depends on the applied washing method.
Use of biodiesel wastewater for biogas and polyhydroxyalkanoates production and for electricity generation.	Biodiesel wastewater is environmentally unfavorable because of high contents of residual oils and greases, esters, COD, BOD, suspended solids, methanol, glycerol, soluble salts, soaps, etc.
Use of biodiesel wastewater as substrate for denitrification of nitrogen-rich wastewaters and for growing algae.	Hard to be degraded naturally because of the presence of microbial growth inhibitor(s).
Treatment of biodiesel wastewater enables removal of various organic pollutants (BOD, COD, grease and oil, methanol, glycerol, etc.), depending on the applied method.	Despite high content of biodegradable organic compounds, biodiesel wastewaters are not suitable for microbial cultivation because of a high pH value and the lack of nutrients important for microbial growth.
Disposable or reusable treated water can be produced by applying the proper biodiesel wastewater treatment.	Biodiesel wastewaters are difficult to treat by traditional methods.
The residual oil, free fatty acids and esters recovered from biodiesel wastewaters can be returned into the biodiesel production enhancing the economics of the overall process.	The use of a single treatment method is usually not enough efficient for reduction the pollutant levels to acceptable limits.
Efficient biodiesel wastewater treatment has a high environmental importance.	Some treatment methods are economically unfavorable in terms of capital investment and operating costs.
	Advanced technologies have not been investigated yet to be applied at large scale for biodiesel wastewater treatment.
	Scale-up of the biodiesel wastewater treatments is not well investigated yet.
Opportunities	**Threats**
Wastewater generation could be minimized by using novel “green” processes for biodiesel production.	As the future demand for biodiesel will increase rapidly, the biodiesel industry could face with a huge amount of wastewater.
Pollutant levels in biodiesel wastewaters can be achieved by modifications of the traditional biodiesel production process.	The different characteristics of biodiesel wastewater depending on the applied biodiesel production process.
The combination of various methods in the multiple-stage biodiesel wastewater treatment can improve the pollutant removal efficiency.	Some biodiesel wastewater treatments can cause generation sludge with low decomposition ability.
Reusable water can be obtained by the integrated treatment of biodiesel wastewater that includes physico-chemical, electrochemical, biological and membrane separation methods.	Environmental risks from large treatment area
Improvement of wastewater treatment by advanced devices and optimization of process conditions.	Disposal of spent adsorbent and hazardous solid wastes.
Development of new, more efficient treatment process for pollutant removal.	Highly corrosive systems in some biodiesel wastewater treatment processes
Screening for efficient less-cost adsorbent and coagulant.	
Development of new processes for converting biodiesel wastewaters into more valuable products and energy.	

directed towards reduced biodiesel wastewater generation. Also, a promising approach is to develop new uses of untreated or partially treated biodiesel wastewater for the production of energy and valuable products. The above mentioned recommendations are environmentally friendly and economically suitable for the overall biodiesel production process.

The possible improvements of the traditional biodiesel production process based on the alkali-catalyzed transesterification reaction that leads to the reduced amount of the biodiesel wastewater generated and the amount of pollutants going to the treatment unit should be considered. No or minimal amount of the biodiesel wastewater is generated in the transesterification processes involving heterogeneous catalysts or enzymes immobilized on solid supports [65]. The crude biodiesel purification step is simplified, since solid particles can be recovered by filtration or decantation or be used in fixed-bed reactors. The same is achieved in the non-catalyzed transesterification processes performed under supercritical conditions [66]. The generation of the biodiesel wastewater could be also avoided or reduced by replacing the water washing of crude biodiesel with dry washing [8,67] or the membrane separation technology [5,68].

Before considering new wastewater treatment options, the traditional biodiesel production process using an alkali catalyst should be analyzed for possible modifications that will result in reduced pollutant levels in the generated biodiesel wastewater. The most important single stage of this traditional process that can reduce the polluted level of the biodiesel wastewater is the introduction of the methanol recovery from crude biodiesel before the water washing stage since methanol is responsible for the majority of the BOD [52]. The methanol recovery from crude biodiesel before its water washing significantly reduced the BOD level, and made the biodiesel wastewater treatment simpler. The methanol excess in crude biodiesel could be removed by distillation or by flash evaporation [69]. Also, the acidification of the biodiesel wastewater with commonly available mineral acids will remove the residual oil, free fatty acids and biodiesel, which will reduce the BOD level and provide a feedstock or a by-product for the biodiesel plant [52].

The biodiesel wastewater treatment process of choice should be balanced between the pollutant removal efficiency and operational costs. The individual treatment processes are shown to be ineffective in treating raw biodiesel wastewaters. Therefore, the right choice is probably an integrated treatment process that includes acidification, coagulation/flocculation or electrocoagulation, a biological process and a membrane separation. Since the investment costs of the integrated process are high, its applicability should be thoroughly examined from the economic point of view. An obstacle for selecting the industrial biodiesel wastewater treatment process is the lack of data on pilot and large-scale plants operated in a continuous mode.

8. Conclusion

Many of the reported methods of the biodiesel wastewater treatment are considered to be an efficient and economical way to reduce its environmental impacts. However, each study started with a different source of the biodiesel wastewater with different

chemical composition. Therefore, it is hard to compare and justify what is the most effective process for treating the biodiesel wastewater.

The chemical coagulation is equally effective at reducing the BOD level and provides a lower operating cost than the electrocoagulation. However, the principle disadvantages of the coagulation process are the requirement of a large treatment area and the contamination of the treated wastewater by chemical coagulants. Thus, the treatment process should be balanced between its treatment efficiency and operational requirements. Biological treatment is promising for possibilities of producing biogas and other valuable products, but further studies are needed.

The effectiveness of each treatment of the biodiesel wastewater should be evaluated and judged in terms of the treatment efficiency and the estimated operating cost. The utilization of the biodiesel wastewater as a potential source of energy is a convenient way of reducing the biodiesel costs and making it more competitive, compared to petroleum diesel. Therefore, the right choice is probably an integration treatment involving acidification, coagulation/flocculation or electrocoagulation and biological processes. The reuse of the final pretreated wastewater is also an interesting option, which might require a combination of primary and secondary treatments with the membrane separation technology.

Without a doubt, the biodiesel production will continue to grow all over the world. The combination of a cleaner technology and environmental engineering, including the appropriate waste treatment, is a good approach to improve the environmental performance of the biodiesel production and to make it more sustainable.

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